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the substrate and a counterelectrode, comprising:

depositing the catalytically active material on a metallic substrate, and

applying an electric direct voltage, on which an alternating voltage is superimposed in such a way that the sign of the sum voltage of direct and alternating voltage does not change, between the substrate and the counterelectrode.

- 18. The process according to Claim 17, wherein the direct voltage at least corresponds to the deposition potential of the catalytically active material.
- 19. The process according to Claim 17, and further comprising providing the substrate, on its surface which is to be coated, with a predetermined surface roughness prior to the deposition.
- 20. The process according to Claim 19, wherein the surface roughness is in the range from 0.3 μm to 10 μm .
- 21. The process according to Claim 17, wherein the catalytically active material is deposited as substantially spherical metal clusters as a result of the alternating voltage component being applied with a frequency of over 50 Hz.
- 22. The process according to Claim 17, wherein the catalytically active material is deposited as substantially

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dendritic metal clusters as a result of the alternating voltage component being applied with a frequency of between 5 and 50 Hz.

- 23. The process according to Claim 17, wherein the catalytically active material is a precious metal, a mixture of precious metals or catalytically active materials, or a mixture of precious metals and catalytically active materials.
- metallic substrate is a stainless steel substrate, and wherein substantially spherical platinum clusters are deposited on said stainless steel substrate from a solution of a platinum compound in 0.1 M H₂SO₄ with a platinum content of approximately 0.1 g/l as a result of a modulated voltage, comprising said direct voltage of approximately 1.3 volts superimposed with said alternating voltage with a voltage swing of 0.3-1 volt and a frequency of 50-100 Hz, being applied between said stainless steel substrate and said counterelectrode.
- 25. The process according to Claim 17, wherein said metallic substrate is a stainless steel substrate, and wherein substantially dendritic platinum clusters are deposited on said stainless steel substrate from a solution of a platinum compound in $0.1~M~H_2SO_4$ with a platinum content of approximately 0.1~g/l as a result of a modulated voltage, comprising said direct voltage of approximately 1.3~volts superimposed with said alternating voltage with a voltage swing of 0.3-1~volt and a

frequency of 5-15 Hz, being applied between said stainless steel substrate and said counterelectrode.

- 26. The process according to Claim 17, wherein said metallic substrate is a stainless steel substrate, and wherein substantially dendritic rhodium clusters are deposited on said stainless steel substrate from a solution of a rhodium compound in 0.1 M $\rm H_2SO_4$ with a rhodium content of approximately 0.2 g/l as a result of a said direct voltage of 1.4-1.6 volt applied between said stainless steel substrate and said counterelectrode and said alternating voltage ($\rm V_{ac}$) with a voltage swing ($\rm V_{PP}$) of 0.3-1.5 volts and a frequency of 5-15 Hz being superimposed.
- 27. The process according to Claim 24, wherein the platinum clusters have sizes between 2 nm and 1 μm .
- 28. The process according to Claim 17, wherein the counterelectrode is formed by platinum-coated titanium.
- 29. The process according to Claim 25, wherein the platinum clusters have sizes between 2 nm and 1 μm.--